Results of Diagnostic of Lithium Ion Batteries after Accelerated Cycle and Calendar Life Test

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Introduction

Lithium-ion batteries have proven to meet and even exceed the power requirement to level the load on the main engine in hybrid electric vehicle (HEV). However, one of the key limitation to this technololgy is its short calendar life. To better understand this issue, Argonne National Laboratory has developed a baseline cell chemistry and build 1 Ah, 18650 high power cells in collaboration with an industrial partner. The cells were subjected to extensive accelerated calendar life and cycle life testing under different state of charge and aging temperatures. At the end of their life, the cells were diagnosis extensively to understand the key factor that limit their life.

Experimental

High-power Type 18650 cells, employing multi-tab current collection, were fabricated by ANL in collaboration with a battery manufacturer. The cells incorporated a $LiNi_{0.8}Co_{0.2}O_2$ positive electrode, a blend of MCMB-6 and SFG-6 graphite for the negative electrode, and a 1 M $LiPF_6$ EC:DEC (1:1) electrolyte. After initial performance characterization, the cells were subjected to elevated temperature calendar and cycle life testing. New and aged cells were disassembled and portions of their electrodes were investigated by means of a reference electrode, Ac-impedance, High Resolution Transmission Electron Microscopy (HRTEM). Scanning Electron Microscopy (SEM), and X-ray Photo-Electron Spectroscopy (XPS) to identify the sources of the impedance rise and power fade of the tested cells.

Results and Discussion

Figure 1 shows the increase in the area specific impedance with aging time of high power 18650 cells that were subjected to both cycle life and calendar life tests at 50°C. The accelerated cycle life test was carried out by charging the cells to 60%SOC and storing them at 50°C, and then applying current pulses that correspond to a nominal capacity of 3%ΔSOC. The accelerated calendar life test, however, was carried out by potentiotating the cells at 60%SOC and storing them at 50°C. The cells were taken from the storage every 2 weeks and a hybrid pulse power characteristics test (HPPC) was carried out to monitor the impedance rise of the cells. The result shows that the area specific impedance of both cell studies subjected to accelearated calendar life and cycle life test increases significantly after 20 weeks storage at 50°C. Micro-reference electrode combined with Ac-impedance study on symetrical cells have confirmed that, in both cases, the main source of impedance rise is due to a significant increase in the charge transfer resistance at the surface of the positive electrode. HRTEM has confirmed a build up of an amorphous and resistive film at the surface of the primarry particles of the positive active material. HR-SEM was very helpful in visualizing a film formation at the surface of the positive electrode, and confirming the break up of the primarry particles of the positive active material. The increase in the ASI of the cells that were subjected to accelerated cycle life test were faster, and reaches almost 60% increase after 8 weeks of storage at 50°C. However, It took almost 20 weeks of aging at the same temperature for the cells that were subjected to accelerated calendar life test to reach the same 60% increased level in the ASI. This result shows clearly that the power fade in the cell subjected to accelerated cycle life is much faster than those subjected to accelerated calendar life. Knowing that in both cases the impedance rise is mainly due to the interfacial resistance increase at the positive electrode, we investigated further the positive active particles from a cell that was subjected to accelerated cycle life. Figure 2 shows HR-TEM of a cross section of a particle taken from a cycle life tested positive electrode. Clear particle craking as well as a significant structural stress were observed. This craking and the structure stress could be due to the fact that during high rate discharge pulsing, more lithium is extracted from the surface than the bulk of the particle causing thus a significant stress on the particle. Electron diffraction taken from the surface and the bulk of the particle shows different unit cell parametters which confirm that the delithiation-lithiation of the lithium at the surface of the particle is different from that at the bulk. The structural stress and the particle craking observed in the positive electrode of a cell that was subjected to accelerated cycle life could account for the fast degradation of the positive electrode that may accelerate the power fade in the cycle life tested cells.

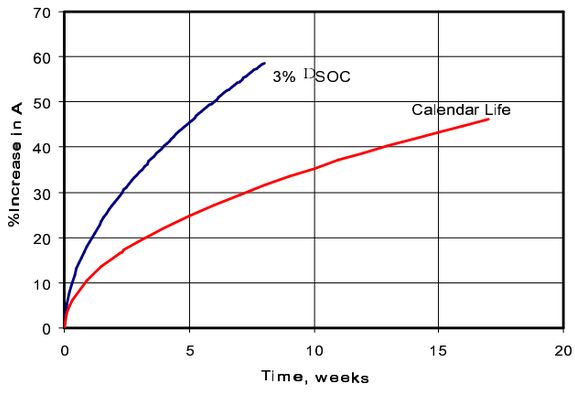

Fig.1 Increase of ASI with aging time at 50°C for cells subjected to accelerated cycle and calendar life test.

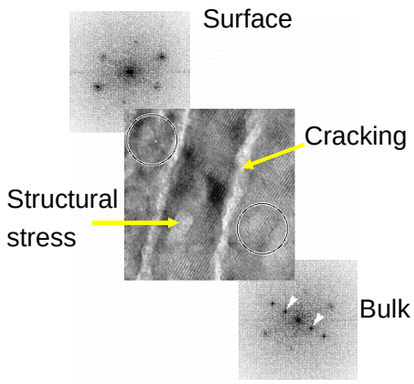

Fig.2 HR-TEM of a positive particle from a cycle life tested cell showing cracking and structural stress.

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